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U1S S1404 S1658

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US 4367316 A

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UK CL (Edition L) **C3M MD MFC MXC**
INT CL^5 **C08L , F16D**
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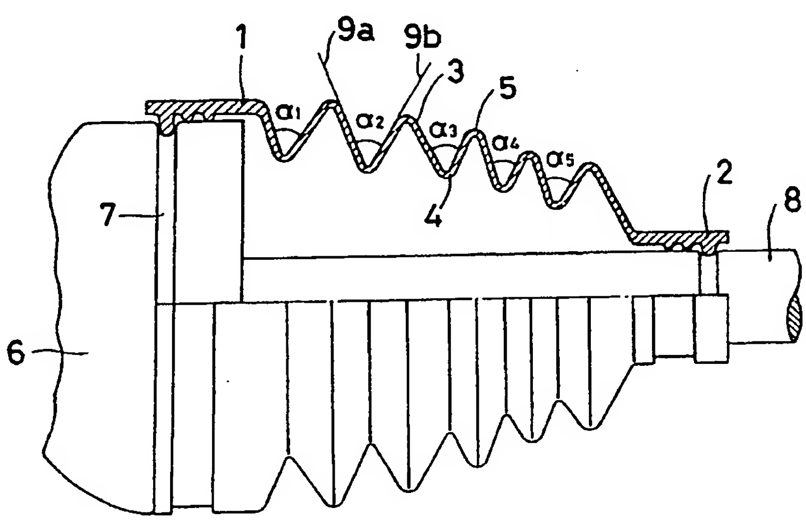
(54) **Joint boot**

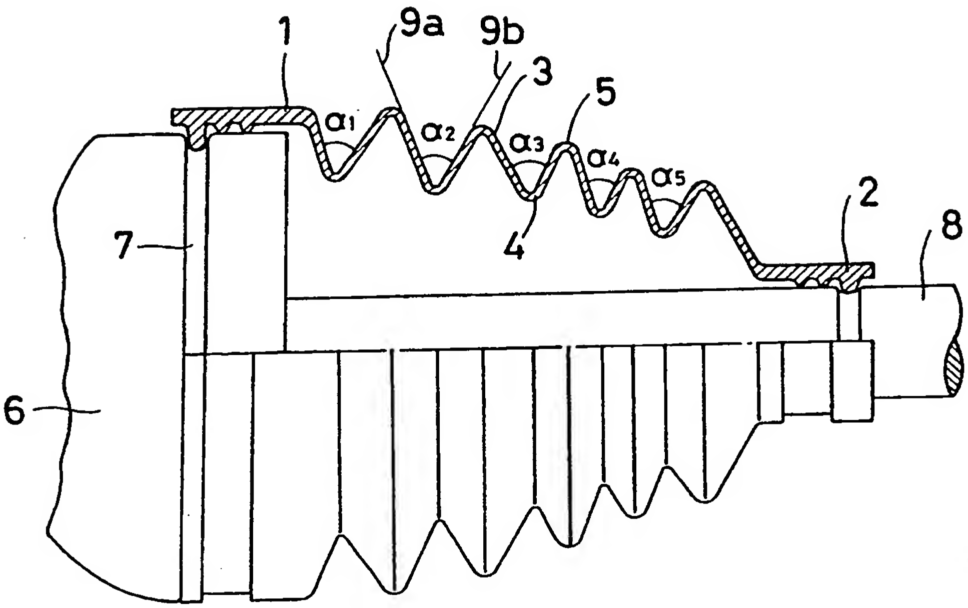
(57) A joint booth 1 is prepared by injection-molding a flexible thermoplastic polyester elastomer composition obtained by blending 20 - 99% by weight of a thermoplastic polyester elastomer and 80 - 1% by weight of a rubber. The modulus of tensile elasticity of the thermoplastic polyester elastomer composition may be in the range of 30 to 400 kgf/cm^2. According to this technique, the flexibility and permanent compression strain resistance, which have been insufficient in the molded joint boot made of a conventional thermoplastic polyester elastomer alone, can be improved. The ratio of the outer diameter of a crest adjacent one end of the boot to that of a crest adjacent the outer end of the boot may be 1 : 1.0 - 0.5.

F I G.1



GB 2 281 301 A

F I G.1



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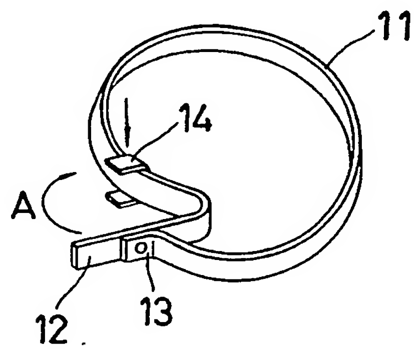

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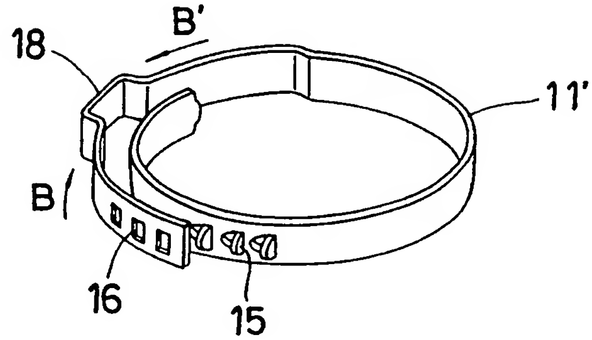
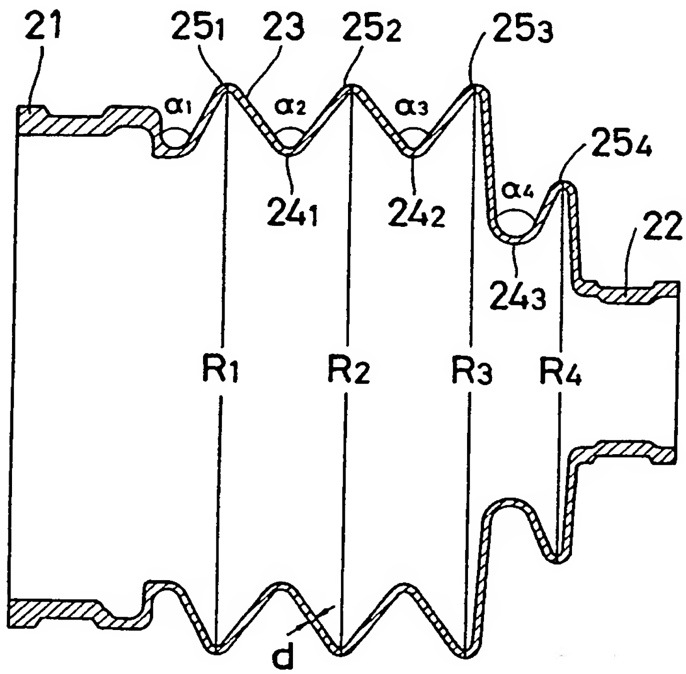

B'
18
11'
B
16
15

F I G.4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25_1
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25_2
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α_1
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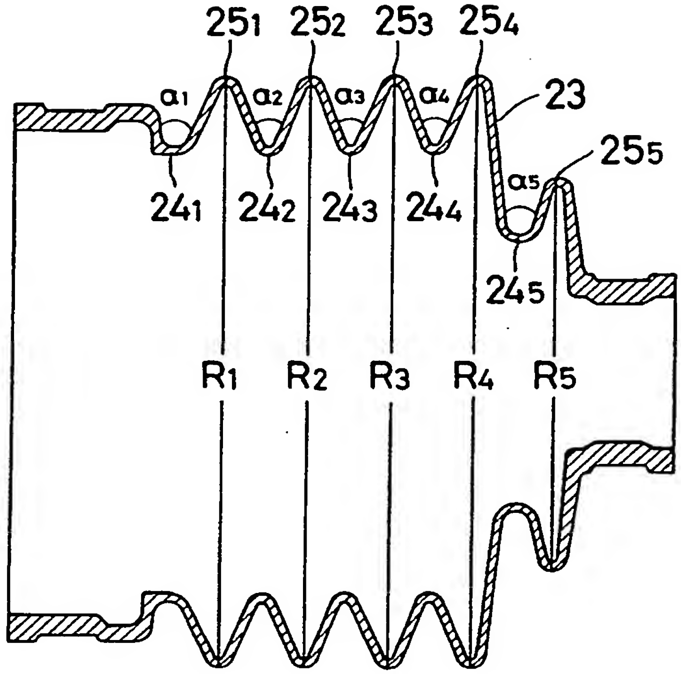
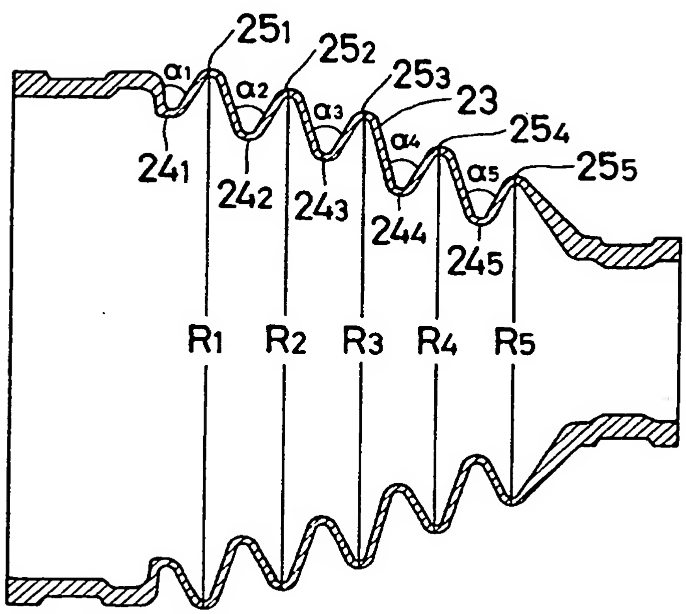
R_1
R_2
R_3
R_4
d

FIG.5



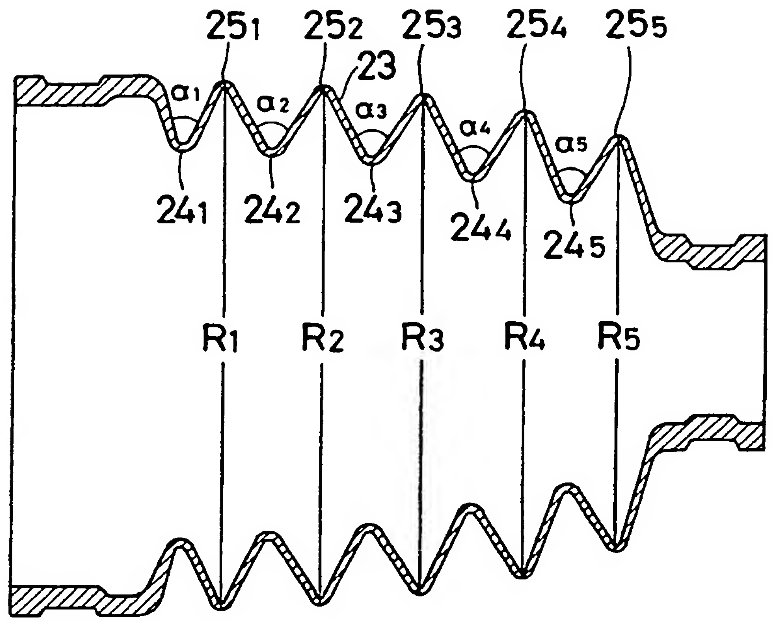
25₁ 25₂ 25₃ 25₄
α1 α2 α3 α4
23
25₅
α5
24₁ 24₂ 24₃ 24₄
24₅
R1 R2 R3 R4 R5

FIG.6



25₁
25₂
25₃
23
25₄
25₅
α1 α2 α3 α4 α5
24₁ 24₂ 24₃ 24₄ 24₅
R1 R2 R3 R4 R5

F I G.7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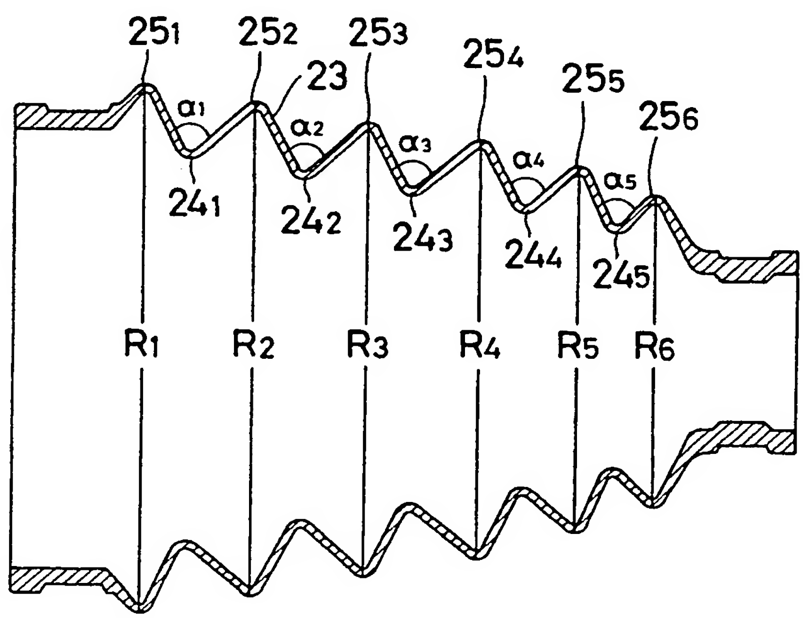
R_5

F I G.8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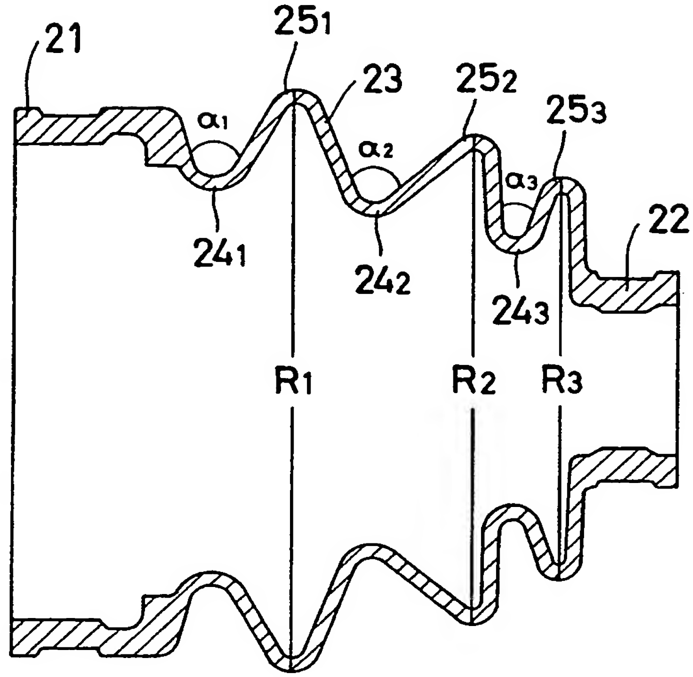
R_5
R_6

FIG.9



DESCRIPTION

"JOINT BOOT"

The present invention relates to a joint boot.

The present invention relates to a joint boot made of a thermoplastic polyester elastomer composition, and more specifically, it relates to a bellows-like joint boot suitable for, for example, a synchromesh joint for automobiles.

Joints found in automobiles or industrial machines are normally covered with a boot in order to protect applied grease or the joint itself from dust.

Such joint boots have been manufactured by injection-molding a rubber material such as a chloroprene rubber.

In recent years, in the field of automobiles, extension of the term of guarantee on parts, for example, from 3 years to 5 years, has become desired, but the above-mentioned rubber material has been found poor in ozone resistance and wear resistance. Under these circumstances, the material of the boots is now being changed from chloroprene rubber to thermoplastic polyester elastomers, and the ozone resistance and the wear resistance of thermoplastic polyester elastomers are so remarkable as to satisfy a guarantee term of 5 years.

However, when it is attempted to mold the boots using thermoplastic polyester elastomers, because its tensile yield

elongation is lower (50-70%) as compared with the conventional rubber material, the length of the bellowed portion of the boots has to be made longer by increasing the number of the crests in the bellows. Furthermore, since the elastomers have a high modulus of elasticity, the thickness of the boot wall must be decreased to a range of about 0.7 to 1.8 mm.

However, in manufacturing the boots having such a structure as mentioned above by injection-molding a thermoplastic polyester elastomer, it is difficult to release the molded article from a mold, because the thermoplastic polyester elastomer has a high modulus of elasticity. Therefore, some special measures, such as the optimization of the undercut ratio and the cutting taper angle for better boot shapes, and the division of the mold core, are necessary. In addition, even if the boot can be molded, plastic deformation tends to occur, and intricate techniques have to be employed to release the boot from a mold. All of these may have negative effects on the productivity of boots.

Accordingly, the manufacture of the boots from thermoplastic polyester elastomers has usually been carried out by blow molding, such as direct blow molding or injection blow molding.

However, in the case of blow molding, there are some problems. For example, in the case of direct blow molding in which a cylindrical parison extruded by a screw or the like

is expanded in a mold to obtain molded articles, the bellows portion of each of the molded boots tends to have nonuniform thicknesses for the crests and valleys, even though the thickness of the extruded parison is controlled. Similarly, in injection blow molding which comprises the steps of injecting a melted resin to form a tube and then blowing air into the formed tube to obtain a molded article, it is still difficult to improve the dimensional accuracy of the internal portion of the molded article. The above-mentioned nonuniform thickness of the molded boots poses serious problems from the viewpoint of their functions and has a large influence on the life of boots.

Even if the above-mentioned problems of the blow molding are solved by controlling the shape of the parison precisely or by an improvement in a molding machine with some special measures for, for example, a mandrel, molded joint boots molded from a thermoplastic polyester elastomer alone give rise to many problems owing to their rigidity when the boots are attached to joints. That is, boots obtained from such a material are difficult to deform owing to their high modulus of elasticity. Therefore, the productivity of these boots deteriorates, and a band fastening the boot becomes subject to large forces when the boot is deformed. Furthermore, boots made of a thermoplastic polyester elastomer alone are poor in permanent compression strain, and thus during the

use of the boot, clamping forces will decline even if fastening is done on a small-diameter portion of the boot.

Therefore, a simple one-touch band for conventional rubber boots cannot be used for a joint boot made of a thermoplastic polyester elastomer alone, and it is necessary to clamp the boot in a special manner using a stronger fixing band. This poses a problem in production processes.

As described above, molded joint boots made of a thermoplastic polyester elastomer alone have excellent mechanical properties, oil resistance, heat resistance and durability, but this material has such high rigidity that injection molding is difficult. Even if the injection molding is possible, product shapes are limited. In the case of blow molding, the thickness of the bellows portion tends to be nonuniform, and in order to secure the durability of the product, special measures have to be taken. In addition, the molded join boots manufactured from this kind of material have poor flexibility and permanent compression strain, and thus simple bands for rubber boots cannot be used.

The present inventors have intensively researched in view of the above-mentioned problems, and as a result, they have found that a thermoplastic polyester elastomer composition which can maintain oil resistance and heat resistance and have improved flexibility and permanent compression

strain can be provided by blending a thermoplastic polyester elastomer with a specific amount of a rubber and, if necessary, by carrying out dynamic crosslinking. As a result of further investigation, they have found that a join boot having a desired shape can be obtained by injection-molding this composition.

Furthermore, the present inventors have made investigations also on the above-mentioned joint boot, and they have found that a join boot having a specific structure has durability comparable to that of a molded joint boot made of a thermoplastic polyester elastomer alone and can be fastened with a simple one-touch band for ordinary rubber boots.

That is, the present invention is directed to a joint boot which is obtained by injection-molding a flexible thermoplastic polyester elastomer composition (C) prepared by blending 20-99% by weight of a thermoplastic polyester elastomer (A) and 80-1% by weight of a rubber (B). Here, "joints" for which the joint boot of the present invention is used include universal joints constituting a coupling portion between a driving shaft and a wheel or a transmission system of driving forces in automobiles or industrial machines.

The above-mentioned thermoplastic polyester elastomer (A) can be a block copolymer comprising high-melting polyester segments and low-melting polymer segments.

An aromatic polyester unit of a high-melting crystal-

line segment (A-1), which is a hard segment, can be formed from an acid component and a glycol component. This acid component is substantially terephthalic acid and/or 2,6-naphthalenedicarboxylic acid. In addition to terephthalic acid and/or 2,6-naphthalenedicarboxylic acid, a small amount of another aromatic dicarboxylic acid, such as isophthalic acid, or an aliphatic dicarboxylic acid, such as adipic acid, sebacic acid, cyclohexane-1,4-dicarboxylic acid or a dimeric acid, can also be added.

Examples of the glycol component constituting the aromatic polyester unit include glycols having 2 to 12 carbon atoms such as ethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, hexanediol and decanediol.

An aliphatic polyether unit constituting a low-melting polymer segment (A-2), which is a soft segment, can be produced from a polyalkylene glycol, and typical examples of the polyalkylene glycol include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and polyethylene glycol-polypropylene glycol block copolymer. Above all, polytetramethylene glycol is preferable. These polyalkylene glycols can be used singly or as a mixture thereof, so long as the ratio of the number of carbon atoms to that of oxygen atoms is within the range of 2 to 4.5.

Another aliphatic polyether unit constituting the low-

melting polymer segment (A-2) can be produced mainly from an aliphatic dicarboxylic acid and a glycol. Examples of the aliphatic dicarboxylic acid, which is the main acidic component of the unit, include succinic acid, adipic acid, sebacic acid and decanedicarboxylic acid. In addition to these aliphatic dicarboxylic acids, a small amount of an aromatic dicarboxylic acid, such as isophthalic acid, may also be added.

The glycol component constituting the aliphatic polyester unit is a glycol having 2 to 12 carbon atoms, and its typical examples include the same compounds as those enumerated for the glycol component which can be used to produce the aromatic polymer unit of the high-melting crystalline segment (A-1).

The aliphatic polyester unit can be obtained by polycondensation of the above-mentioned aliphatic dicarboxylic acid and glycol component in a usual manner, and it may be a homopolyester, a copolymer polyester, or a polylactone (e.g., poly-ε-caprolactone) obtained by the ring opening polymerization of a cyclic lactone. No particular restriction is placed on the upper limit of a melting point of the low-melting polymer segment (A-2), but it is usually 130°C or less, preferably 100°C or less. In addition, the molecular weight of the low-melting polymer segment (A-2) is normally between 400 and 6,000.

A composition ratio of the high-melting crystalline segment (A-1) to the low-melting polymer segment (A-2) in the thermoplastic polyester elastomer (A) is preferably between 95/5 and 5/95, more preferably between 70/30 and 30/70. The particularly preferable thermoplastic polyester elastomer (A) has a softening point of 100°C or more.

A polyester block copolymer which can be particularly preferably used as the thermoplastic polyester elastomer (A) can be formed using polytetramethylene terephthalate or polytrimethylene terephthalate-2,6-naphthalate as the high-melting crystalline segment (A-1), and a polyether, such as polytetramethylene glycol, or a polyester, such as polytetramethylene adipate and poly-ε-caprolactone, as the low-melting polymer segment (A-2). Alternatively, a copolymer which is obtained by the copolymerization of a polycarboxylic acid, a polyfunctional hydroxy compound or an oxyacid can be used as a part of the dicarboxylic acid or the glycol. These polyfunctional components effectively function as a viscosity-increasing component when they are copolymerized in an amount of 3 mol% or less. Examples of the polyfunctional components include trimellitic acid, trimesic acid, pyromellitic acid, benzophenonetetracarboxylic acid, butanetetracarboxylic acid, glycerin, pentaerythritol, and esters and acidic anhydrides thereof.

The thermoplastic polyester elastomer (A) can be pre-

pared by a usual polymerization process. As suitable polymerization processes, there are a method which comprises the steps of heating an aromatic dicarboxylic acid or its dimethyl ester and a diol which can form a low-melting segment to about 150-260°C in the presence of a catalyst so as to carry out an esterification reaction or an ester exchange reaction, and carrying out a polycondensation reaction while excessive low-molecular diol is removed under vacuum; a method which comprises the steps of mixing a prepolymer which forms a high-melting polyester segment and a prepolymer which forms a low-melting polymer segment, which are prepared in advance, with a bifunctional chain extender which can react with end groups of these prepolymers, allowing the mixture to react, and then removing volatile components under high vacuum, so as to obtain a desired thermoplastic polyester elastomer; and a method which comprises the steps of heating and mixing a lactone and a highly polymerized high-melting polyester, and then bringing the lactone subject to an ester exchange reaction while it is subjected to ring-opening polymerization, so as to obtain a desired thermoplastic polyester elastomer.

As the above-mentioned rubber (B), various kinds of synthetic rubbers and natural rubbers can be used singly or in combination. Preferable examples of rubber (B) include polar diene-based rubbers, hydrogenated polar diene-based rubbers, acrylic rubbers, hydrin rubbers, urethane rubbers,

chlorophosphagen rubbers, thermoplastic polyurethane elastomers and thermoplastic polyamide elastomers. In addition, silicone rubbers and fluorine-containing rubbers can also be used preferably as rubber (B) because of their oil resistance.

In the present invention, particularly preferable examples of rubber (B) include non-halogenated diene-based rubbers, hydrogenated non-halogenated diene-based rubbers, and epichlorohydrin rubbers. Typical examples of rubber (B) include acrylonitrile-butadiene copolymer rubber, hydrogenated acrylonitrile-butadiene copolymer rubber, hydrogenated acrylate-butadiene copolymer rubber, and ethylene-propylene copolymer rubber.

In the thermoplastic polyester elastomer composition (C), a blend ratio between the thermoplastic polyester elastomer (A) and rubber (B) is restricted as: component (A) : component (B) = 99-20 : 1-80% by weight; preferably 95-51 : 5-49% by weight; more preferably 85-55 : 15-45% by weight. When component (A) is excessive, the content of component (B) becomes small as a result, so that the flexibility and the permanent compression strain of composition (C) may not be sufficiently improved. For sufficient improvements, it is preferred that the content of component (A) is 95% by weight or less. When the amount of component (A) is less than 20% by weight, the resultant composition (C) is poor in workabil-

ity and fluidity. Such composition (C) is not preferable as a material for the joint boot. As the material for injection molding, it is particularly preferable that the content of component (A) is 51% by weight or more.

While the thermoplastic polyester elastomer composition (C) of the present invention can be obtained by simply blending the thermoplastic polyester elastomer (A) and rubber (B), dynamic crosslinking is effected for obtaining composition (C) with a higher performance. The dynamic crosslinking is a technique developed by W. M. Fischer et al. of Uniroyal Inc. and A. Y. Coran et al. of Monsanto Chemical Co., and this technique comprises the steps of blending a rubber with the matrix of a thermoplastic resin, and then kneading them together with a crosslinking agent to make the rubber highly crosslinked and disperse the rubber finely.

Crosslinking agents which can be used in the dynamic crosslinking include peroxides, resin crosslinking agents, and sulfur, which are crosslinking agents used for ordinary rubbers. Typical examples of the crosslinking agent include crosslinking agents, crosslinking auxiliaries and crosslinking accelerators mentioned in "Handbook of Crosslinking Agents (*Kakyozai Handobukku*)" (Shinzo Yamasita and Tousuke Kaneko, Taiseisha Co., Ltd.).

That is, examples of the crosslinking agent which can be preferably used in the present invention include 1,3-di(t-

butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexine-3, and t-butylcumyl peroxide.

The amount of the crosslinking agent to be added depends upon a required performance of composition (C) and the kind of crosslinking agent, but in general, it is in the range of 0.01 to 8 parts by weight for 100 parts by weight of rubber (B). When the amount of the crosslinking agent is more than 8 parts by weight, a further crosslinking effect cannot be expected any more, which is not economical. In addition, an undesirable side reaction such as decomposition of the polymer tends to occur. When it is less than 0.01 part by weight, the crosslinking cannot be sufficiently achieved.

The dynamic crosslinking in the present invention can be carried out by kneading the above-mentioned components with the aid of an extruder, a Banbury mixer, a kneader or a combination thereof. However, for high productivity, it is most preferable to continuously produce composition (C) by the use of a twin-screw extruder. In such a case, in the middle of the operation of the extruder, the plasticizer and the crosslinking agent are added.

In the case of the thermoplastic polyester elastomer (A) alone, its hardness H_D is 45 points or more (H_S is 96 points or more), and its modulus of tensile elasticity at

ordinary temperature (23°C ± 5) is 600 kgf/cm^2 or more. On the contrary, the hardness H_D of the thermoplastic polyester elastomer composition (C) which is blended with rubber (B) is in the range of 20 to 44 points (H_s is 60-95 points), and its modulus of tensile elasticity is 400 kgf/cm^2 or less, which means that composition (C) is soft.

In the present invention, the particularly preferable thermoplastic polyester elastomer composition (C) has a modulus of tensile elasticity of 30 to 400 kgf/cm^2. The thermoplastic polyester elastomer composition (C) can be obtained by dynamically crosslinking two components: a thermoplastic polyester elastomer (A) obtained by using polytetramethylene terephthalate or polytrimethylene terephthalate-2,6-naphthalate as the high-melting crystalline segment (A-1) and a polyether, such as polytetramethylene glycol, or a polyester, such as polytetramethylene adipate or poly-ε-caprolactone, as the low-melting polymer segment (A-2); and a rubber (B) (component (B)), such as acrylonitrile-butadiene copolymer rubber, hydrogenated acrylonitrile-butadiene copolymer rubber, hydrogenated acrylate-butadiene copolymer rubber or ethylene-propylene copolymer rubber; with a ratio of component (A) : component (B) = 85-55% : 15-45% by weight, in the presence of the above-mentioned crosslinking agent.

The employment of composition (C) having a modulus of

tensile elasticity of 30-400 kgf/cm^2 makes it possible to obtain a molded joint boot having good expansion resistant properties against rotation and negative-pressure resistant properties. Furthermore, the employment of composition (C) having a modulus of tensile elasticity of 50-390 kgf/cm^2 makes it possible to improve the caulking properties of the molded boot with a one-touch band. Additionally, in order to obtain the molded joint boot having the good expansion resistant properties against rotation and negative-pressure resistant properties, the JIS A hardness of composition (C) is in the range of 60 to 95 points, preferably 65 to 95 points. (JIS stands for Japanese Industrial Standard.)

That is, when the modulus of tensile elasticity and the hardness of composition (C) are less than the above-mentioned ranges, the expansion resistant properties against rotation are poor, and the bellows portion of the molded boot is expanded with a high-speed rotation due to centrifugal forces under rotation. In addition, the negative-pressure resistant properties are poor, and the internal pressure inside the molded boot lowers with a drop in ambient temperature, so that the long wall of the bellows may become "bitten into" or bent down and caught.

On the other hand, the modulus of tensile elasticity and the hardness of composition (C) are above the above-mentioned ranges, the object of the present invention cannot

be achieved.

The tensile breaking strength of the thermoplastic polyester elastomer composition (C) is preferably in the range of 50 to 300 kgf/cm^2, more preferably 60 to 280 kgf/cm^2, most preferably 70 to 250 kgf/cm^2. When the tensile breaking strength is less than 50 kgf/cm^2, the strength required for the molded joint boot is insufficient, and when it is more than 300 kgf/cm^2, the content of the rubber must be limited to a minimum, and sufficient flexibility cannot be obtained.

In order to make it possible to use simple one-touch bands, the permanent compression strain of composition (C) is preferably 80% or less (JIS K-6301, 120°C, 22 hours), more preferably 75% or less, most preferably 70% or less. When this requirement is met, the band can be prevented from disengaging out of a fixing portion with small diameter, as joint boots are often fastened to such a fixing portion.

With regard to the measurement of hardness, the hardness H_D is measured in accordance with ASTM D2240 using a type D Shore durometer, and the hardness H_s is measured in accordance with JIS K630 using a JIS A type Shore durometer. In addition, the modulus of tensile elasticity is measured as a value for the dynamic modulus of tensile elasticity at 23 ± 2°C by a forced-vibration non-resonance process. The measurement of the modulus of tensile elasticity is carried out

by applying sinusoidal-wave strain having a frequency of 10 Hz and a displacement amplitude of 3 μm to a test piece having a width of about 2 mm, a thickness of about 1 mm and a length of about 30 mm, measuring dynamic stress, dynamic displacement and phase angle, and then determining the dynamic modulus of tensile elasticity in accordance with the following formula:

$$E^* = \frac{DF \times 980.6 \times CD}{DD \times W \times T} 1.01972 \times 10^{-3} \ (kgf/cm^2)$$

$E' = E^*\cos(P)$ (kgf/cm^2)

E^* = complex modulus of elasticity (kgf/cm^2)

E' = dynamic modulus of tensile elasticity (kgf/cm^2)

CD = length of specimen (cm)

DF = dynamic stress (gramf)

DD = dynamic displacement (cm)

P = phase angle (degrees)

W = width of specimen (cm)

T = thickness of specimen (cm)

In the present invention, the thermoplastic polyester elastomer composition (C) is injection-molded. The employment of the injection molding leads to the molded joint boot having a uniform thickness.

The fluidity of composition (C) at the time of the injection molding is preferably at an MFR value of 0.1 g/min (fluidity measured at 230°C under a load of 10 kg) or more,

as the fluidity of a melted polymer is measured in accordance with JIS K-7210. When the MFR value is less than 0.1 g/min, the fluidity of composition (C) is poor in a mold, so that the good molding cannot be achieved.

Conditions of the above-mentioned injection molding are as follows:

Rotational speed of a screw:	100-400 rpm,
Temperature of cylinder:	180-230°C
Temperature of nozzle:	about 210°C
(around a melting point of the composition)	
Injection pressure:	400-1,600 kgf/cm^2
Injection time:	1-3 seconds
Cooling time:	15-60 seconds
Temperature of mold:	20-50°C

According to the present invention described above, the joint boot having a desired shape and structure can be provided.

No particular restriction is put on the shape or structure of the joint boot of the present invention, but the joint boot having the structure described below has durability comparable to that of a joint boot made from a thermoplastic polyester elastomer alone and can be fixed by a simple one-touch band for a rubber boot.

That is, the present invention is also directed to a joint boot provided with a bellows portion 3 having valleys 4

and crests 5 between a large-diameter opening 1 and a small-diameter opening 2 as shown in Fig. 1, said joint boot being characterized in that angles α_1, α_2, α_3, α_4 and α_5 each of which is formed by the slant face on the large-diameter opening side of a valley and the slant face on the small-diameter opening side of another valley adjacent thereto are substantially equal to each other between different valleys, and a ratio of the outer diameter of a crest on the large-diameter opening side to that of another crest adjacent thereto on the small-diameter opening side is in the range of 1 : 1.0-0.50.

In Fig. 1, reference numeral 6 denotes a joint socket, 7 an annular groove, and 8 a driving shaft. The angle made by the two slant faces of each valley (hereinafter referred to as "valley angle") can be defined as an angle α (α_2 in Fig. 1) made by straight lines drawn along the two slant faces 9a, 9b of the valley.

If the above-mentioned joint boot is a boot used for synchromesh joints in automobiles, a maximum envelope curve simply drawn passing the crests of the bellows is to be determined in view of a minimum non-interfering space between the boot itself and parts, such as a stabilizer, in the vicinity of the boot under ordinary conditions and under a maximum deformation around the space provided for the disposition of the boot for the synchromesh joint in an automo-

bile. In addition, the length of the bellows, the number of the crests, and the thickness of the bellows are decided on the basis of a volume of the folded bellows and a volume of the expanded bellows under the conditions of a maximum operational angle.

Therefore, the number of the crests in the bellows portion of the joint boot of the present invention is preferably 4 or more in consideration of the expanded volume of the bellows at the maximum operational angle. At the same time, in consideration of the volume of the folded bellows when compressed, the number of the crests is preferably 9 or less, in order to avoid large friction when the thickness of the bellows wall is 0.5 mm or more. Therefore, the number of the crests of the bellows portion should be in the range of 4 to 9, preferably 4 to 8, more preferably 5 to 7.

In the above-mentioned joint boot, the angles each of which made by the slant face on the large-diameter opening side of a valley and the slant face on the small-diameter opening side of another valley adjacent thereto is substantially equal to each other among different valleys, and the ratio of the outer diameter of a crest on the large-diameter opening side to that of another crest adjacent thereto on the small-diameter opening side is in the range of 1 : 1.0-0.50. Therefore, the respective walls of the bellows portion uniformly contact with each other under the maximum deformation

of the joint boot, whereby excellent wear resistance can be obtained.

The external diameter of the maximum crest of the joint boot is preferably up to 1.2 times as large as the external diameter of the outer ring of the joint or smaller in view of the limited space where the molded joint boot is attached.

The thickness (d) of the bellows portion is preferably in the range of 0.5 to 2.5 mm in view of the fluidity of the melted resin at the time of the injection molding and judging from the fact that the modulus of tensile elasticity of the thermoplastic polyester elastomer composition (C) is 400 kgf/cm^2 or less. When the thickness of the bellows portion is less than 0.5 mm, the expansion resistant properties against rotation and resistant properties against negative pressures become poor, and the joint boot has functional problems. When it is more than 2.5 mm, large friction occurs at the maximum operational angle, even if the number of the crests in the bellows portion is set to 3.

The joint boot of the present invention can be attached to the joint body by fastening its large-diameter portion 1 and small-diameter portion 2 to the joint body with one-touch bands (hereinafter referred to as "band A") shown in Fig. 2.

The band A shown in Fig. 2 has a curved portion 11 formed by curving a steel plate of about 0.3 mm in thickness and about 7 mm in width, and an extended portion 12 formed by

extending one end portion of the curved member 11. This extended portion 12 is screwed on another end portion 13 of the curved member 11. The fixation of the joint boot by this band A can be done first by folding the extended portion 12 in a direction shown by arrow A, and then by folding two lugs 14 provided at a predetermined position of the curved member 11. This serial operation can be simply carried out by hand, and so the attachment of the joint boot of the present invention is extremely easy.

A one-touch band (hereinafter referred to as "band B") shown in Fig. 3 has a curved portion 11' formed by curving a steel plate of 0.4-0.7 mm in thickness and about 10 mm in width, lugs 15 provided on one end portion of the curved portion 11', and engaging holes 16 which are formed at another end portion thereof and which can be engaged with the lugs 15. To fasten the joint boot with this band B, first the lugs 15 are engaged in the engaging holes 16, and then a cramping lug 18 formed at a predetermined position in the curved portion 11' simultaneously is pinched from both directions indicated by arrows B to caulk. The band B can preferably be used to fix the boot comprising the thermoplastic polyester elastomer alone such as Hytorel (trademark). The boot comprising the usual thermoplastic polyester elastomer alone has a large modulus of elasticity of 600 kgf/cm^2 or more, and so it is necessary that the boot band has a thick-

ness of about 0.5-0.7 mm, and suitable caulking tools and many steps are required for caulking operations.

For the joint boot of the present invention, the thermoplastic polyester elastomer composition which is flexible owing to the added rubber is used, and it is therefore possible to obtain a modulus of elasticity of 400 kgf/cm^2 or less. Use of the band A for ordinary rubber boots is possible for the joint boot of the present invention, and hence significant improvements can be made in manufacturing processes. That is, the joint boot of the present invention can be fixed to the joint body without using the band B.

As means for evaluating the joint boot, there exist, loosely categorized, a durability test, a negative pressure test, and a rotary expansion test. The durability test is carried out by first applying grease on the boot, continuously driving the boot at an atmospheric temperature of -5°C at a joint angle of 30 degrees at a rotational speed of 400 rpm for 50 hours, and then determining the time (in hours) passing before the breakage of the boot. This test is terminated when any breakage does not occur even after 50 hours, and in this case, it is evaluated that the boot durability is satisfactory. In the negative pressure test, the pressure in the joint is made negative, and the shape and material of the boot are then evaluated on the basis of quantitative boot deformation. Furthermore, in the rotary expansion test, the

amount of expansion of the boot is measured by means of an optical microscope, while it is rotated at a high speed.

The joint boot of the present invention which can be obtained by injection-molding a thermoplastic polyester elastomer to which a rubber is blended has excellent fundamental characteristics, such as strength, permanent compression strain, heat resistance, weather resistance, coldness resistance, and grease resistance, as well as practical characteristics, such as fatigue resistance and wear resistance, and in addition, it is very flexible. Therefore, according to this joint boot, the flexibility and the permanent compression strain resistance, which have been found insufficient in molded joint boots made of a conventional thermoplastic polyester elastomer alone, can be improved. Because it is flexible, the joint boot of the present invention can be easily released from a mold even if it is formed into an intricate shape. This makes it possible to utilize injection molding.

Moreover, according to the present invention, the molded joint boot can be manufactured by the injection molding, and therefore the degree of freedom of a joint boot design can be extended, and dimensional accuracy can be secured, whereby the joint boot having a uniform wall thickness can be obtained.

In addition, according to the joint boot having a

particular shape of the present invention, durability can be greatly improved, and the attachment of the boot to the joint is easy during manufacturing processes because it is flexible. Furthermore, since the permanent compression strain of the joint boot is small, the boot can be fixed by a simple one-touch band for rubber boots. In consequence, the performance of the joint boot of the present invention can be remarkably improved, as compared with a joint boot made of a conventional thermoplastic polyester elastomer alone.

The present invention will now be further described, by way of example, with reference to several examples and the accompanying drawings, in which:-

Fig. 1 is a semi-sectional view of a joint boot of the present invention which is mounted on a joint.

Fig. 2 is a perspective view of a one-touch band for fixing the joint boot of the present invention.

Fig. 3 is a perspective view of a one-touch band which can be preferably used to fix the boot comprising a thermoplastic polyester elastomer alone.

Fig. 4 is a sectional view of the molded joint boot obtained in Example 1.

Fig. 5 is a sectional view of the molded joint boot obtained in Example 2.

Fig. 6 is a sectional view of the molded joint boot obtained in Example 3.

Fig. 7 is a sectional view of the molded joint boot obtained in Example 4.

Fig. 8 is a sectional view of the molded joint boot obtained in Example 5.

Fig. 9 is a sectional view of the molded joint boot obtained in Comparative Example 1.

Example 1

A thermoplastic polyester elastomer (trade name PIBIFLEX 46M, manufactured by Enichem Polymeri Co., Ltd.) and an acrylonitrile butadiene rubber (trade name JSR NBR N230SV, manufactured by Japan Synthetic Rubber Co., Ltd.; hereinafter referred to as "NBR") were simply kneaded at 210°C at a rotational speed of 200 rpm in ratios shown in Table 1 using a biaxial extruder to prepare a composition (composition No. 3 in Table 1) in the form of pellets, and other compositions (composition Nos. 1 and 2 in Table 1) was also prepared in the form of pellets under the same conditions except that a crosslinking agent was added during the kneading step to carry out dynamic crosslinking. The thus obtained pellets were sufficiently dried, and they were then molded into sheets having a thickness of 2 mm at 210°C by an injection molding machine, and the molded sheets were then subjected to

various tests.

In this connection, physical properties of a thermoplastic polyester elastomer alone (composition No. 4) are also shown for comparison in Table 1.

The tests utilized for the evaluation of the physical properties were as follows:

(1) Fluidity: MFR, 230°C × 10 kg

(2) Hardness H_S: JIS K-6301 JIS A hardness

H_D: ASTM D-2240 Shore D hardness

(3) Tensile strength T_B: JIS K-6301 JIS No. 3 dumbbell

(4) Tensile elongation E_B: JIS K-6301 JIS No. 3 dumbbell

(5) Modulus of tensile elasticity: Ditto

(6) Thermal aging resistance: JIS K-6301

Tensile strength after 300 hours at 120°C was measured using a gear-type aging test machine, and the thermal aging resistance was represented by the change (%) of measured tensile strength of the specimen before and after exposure to heat.

(7) Oil resistance: JIS K-6301

Tensile strength after immersion in JIS No. 3 oil at 120°C for 70 hours was measured, and the oil resistance was represented by the change (%)

of measured tensile strength of the specimen before and after the immersion.

(8) Wear resistance: ASTM D 1044,
Taper wear CS-17 wheel, 1,000 g weight

(9) Permanent compression Strain: JIS K-6301,
120°C, 22 hours

Table 1

	Composition No. 1	2	3	4
Blend				
TPEE[1] (parts by wt.)	75	65	75	100
NBR[2] (parts by wt.)	25	35	25	
Auxiliary-1[3] (parts by wt.)	0.6	0.5		
P.O[4] (parts by wt.)	0.3	0.3		
Physical Properties				
MFR (g/min)	10	18	40	>100
H_S (JIS A)	88	84	85	97
H_D (Shore D)	40	35	37	46
T_B (kgf/cm^2)	170	160	120	220
E_B (%)	680	700	600	710
Modulus of tensile elasticity (kgf/cm^2)	360	350	300	640
Thermal Aging Resistance (%)	3	-2	-15	5
Oil Resistance (%)	4	3	-15	3
Wear Resistance (10^3 times, mg)	50	51	54	48
Permanent Compression Strain (%)	58	54	75	100

1): PIBIFLEX 46M (Enichem Polymeri Co., Ltd.)
2): JSR NBR N230SV (Japan Synthetic Rubber Co., Ltd.)
3): PALNOK PM (Ohuchi Shinko Chemical Industries Co., Ltd.)
4): KAYAHEXA AD (Kayaku Akzo Co., Ltd.)

Next, compositions No. 1 to 3 shown in Table 1 were injection-molded under the following conditions to obtain molded joint boots I having a shape shown in Fig. 4.

· Conditions of the injection molding

Rotational speed of screw: 100 rpm

Temperature of cylinder: 210°C

Temperature of nozzle: 210°C

Injection pressure: 800 kgf/cm^2

Injection time: 2 seconds

Cooling time: 20 seconds

Temperature of mold: 40°C

Each of the thus molded joint boots 1 was bellows having a large-diameter opening 21 and a small-diameter opening 22 and a bellows portion 23 therebetween, as shown in Fig. 4. In the bellows portion 23, four valleys 24_1, 24_2, 24_3 and 24_4 as well as four crests 25_1, 25_2, 25_3 and 25_4 were formed, and valley angles α_1, α_2, α_3 and α_4 of the four valleys 24 were all substantially equal to each other. The external diameters of the crests 25_1, 25_2, 25_3 and 25_4 were substantially equal to each other, and the ratio of the external diameter (R_3) of the crest 25_3 to the external diameter (R_4) of the crest 25_4 was about 3:2. In addition, the thickness (d) of the bellows portion was 1.0 mm.

After the injection molding properties of the molded joint boots 1 were evaluated, each joint boot 1 was mounted

on a synchromesh joint for automobiles, as shown in Fig. 1. Next, the clamping properties and the life of the boots were evaluated.

The grading scheme for evaluation was as follows:

1. Injection molding properties:

The injection molding properties were evaluated to be good when no short shots were present and appearance was not noticeably bad (i.e., neither flow marks nor delamination were present).

2. Clamping properties:

The clamping properties were evaluated in accordance with the following grading scheme on the basis of conditions at the time of clamping the large-diameter opening 21 and the small-diameter opening 22 using band A shown in Fig. 2 and band B in Fig. 3.

The evaluation of "o" was given in the following cases:

For band A: If the boot could be cramped easily by hand and a problem such as poor sealing properties was not present.

For band B: If the boot could be cramped using a caulking tool and a problem such as poor sealing properties was not present.

The evaluation of "x" was given in the following cases:

For band A: If cramping by hand was impossible and a caulking tool was required, or

if the band was broken at the cramping, or

if problems such as poor sealing properties were found.

For band B: If the cramping was impossible even using the caulking tool, or

if the band was broken, or

if problems such as poor sealing properties were found.

3. Life:

The life of the boot specimen cramped by band A was evaluated under the following conditions in the same manner as described above:

Temperature of atmosphere: -5°C

Joint actuation angle: 30 degrees

Rotational speed: 400 rpm

Evaluation: A boot in which grease was applied was continuously driven for 50 hours, and the time (hours) before the breakage of the boot was determined. This test was terminated when any breakage did not occur even after 50 hours, and in such a case it was evaluated that the boot durability was satisfactory. The evaluation results of the physical properties are set forth in Table 2.

<u>Example 2</u>

The same procedure as in Example 1 was carried out to injection-mold a joint boot II which was almost identical to

the molded joint boot I except that the bellows portion 23 was provided with five valleys 24_1, 24_2, 24_3, 24_4 and 24_5 as well as five crests 25_1, 25_2, 25_3, 25_4 and 25_5, as shown in Fig. 5, and physical properties of the boot were then evaluated. The results of the evaluated physical properties are set forth in Table 2.

Example 3

The same procedure as in Example 1 was carried out to obtain about the same joint boot III as the molded joint boot I except that a bellows portion 23 was provided with five valleys 24_1, 24_2, 24_3, 24_4 and 24_5 as well as five crests 25_1, 25_2, 25_3, 25_4 and 25_5, and external diameter ratios of the crests were $R_1:R_2 = 1:0.92$, $R_2:R_3 = 1:0.913$, $R_3:R_4 = 1:0.84$ and $R_4:R_5 = 1:0.83$, as shown in Fig. 6. The results of evaluated physical properties are set forth in Table 2.

Example 4

The same procedure as in Example 1 was carried out to obtain a joint boot IV which was almost identical to the molded joint boot I except that a bellows portion 23 was provided with five valleys 24_1, 24_2, 24_3, 24_4 and 24_5 as well as five crests 25_1, 25_2, 25_3, 25_4 and 25_5, and external diameter ratios of the crests were $R_1:R_2 = 1:0.973$, $R_2:R_3 = 1:0.972$, $R_3:R_4 = 1:0.928$ and $R_4:R_5 = 1:0.877$, as shown in Fig. 7. The results of evaluated physical properties are set forth in Table 2.

Example 5

The same procedure as in Example 1 was carried out to obtain a joint boot V which was almost identical to the molded joint boot I except that a bellows portion 23 was provided with five valleys 24_1, 24_2, 24_3, 24_4 and 24_5 as well as six crests 25_1, 25_2, 25_3, 25_4, 25_5 and 25_6, and the external diameter ratios of the crests were $R_1:R_2$ = 1:0.932, $R_2:R_3$ = 1:0.927, $R_3:R_4$ = 1:0.922, $R_4:R_5$ = 1:0.864 and $R_5:R_6$ = 1:0.843, as shown in Fig. 8. The results of evaluated physical properties are set forth in Table 2.

Table 2

	Molded Materials No.		
	1	2	3
Example 1 (Molded Article I)			
Injection Moldability	Good	Good	Good
Band Clamp Properties			
Band A Type	o	o	o
Band B Type	o	o	o
Life (band A) (hrs)	40	40	40
Example 2 (Molded Article II)			
Injection Moldability	Good	Good	Good
Band Clamp Properties			
Band A Type	o	o	o
Band B Type	o	o	o
Life (band A) (hrs)	50	50	50
Example 3 (Molded Article III)			
Injection Moldability	Good	Good	Good
Band Clamp Properties			
Band A Type	o	o	o
Band B Type	o	o	o
Life (band A) (hrs)	50	50	50
Example 4 (Molded Article IV)			
Injection Moldability	Good	Good	Good
Band Clamp Properties			
Band A Type	o	o	o
Band B Type	o	o	o
Life (band A) (hrs)	50	50	50
Example 5 (Molded Article V)			
Injection Moldability	Good	Good	Good
Band Clamp Properties			
Band A Type	o	o	o
Band B Type	o	o	o
Life (band A) (hrs)	50	50	50

Comparative Example 1

About the same procedure as in Example 1 was carried

out except that composition No. 4 shown in Table 1 was used, to obtain a joint boot VI shown in Fig. 9. In this obtained joint boot VI, a bellows portion 23 was provided with three valleys 24_1, 24_2 and 24_3 as well as three crests 25_1, 25_2 and 25_3, valley angles α_1, α_2 and α_3 were quite different from each other, and external diameter ratios of the crests were $R_1 : R_2 = 1 : 0.84$ and $R_2 : R_3 = 1 : 0.82$. The results of evaluated physical properties are set forth in Table 3.

Comparative Examples 2 to 6

Under the same conditions as Examples 1 to 5 except that composition No. 4 shown in Table 1 was used, attempts were made to injection-mold joint boots having the same shape as in molded joint boots obtained in Examples 1 to 5, but each boot was not released from a mold, while the shape of the boot was maintained. The results of evaluated physical properties are set forth in Table 3.

Table 3

	Molded Material No. 4
Comparative Example 1 (Molded Article VI)	
Injection Moldability	Good
Band Clamp Properties	
Band A Type	×
Band B Type	o
Life (band A) (hrs)	-
Comparative Example 2 (Molded Article I)	
Injection Moldability	Bad Permanent deformation was present.
Band Clamp Properties	
Band A Type	×
Band B Type	o
Life (band A) (hrs)	-
Comparative Example 3 (Molded Article II)	
Injection Moldability	Bad Permanent deformation was present.
Band Clamp Properties	
Band A Type	×
Band B Type	o
Life (band A) (hrs)	-
Comparative Example 4 (Molded Article III)	
Injection Moldability	Bad Permanent deformation was present.
Band Clamp Properties	
Band A Type	×
Band B Type	o
Life (band A) (hrs)	-

Table 3 (Continued)

	Molded Material No. 4
Comparative Example 5 (Molded Article IV)	
Injection Moldability	Molding was impossible.
Band Clamp Properties	
Band A Type	-
Band B Type	-
Life (band A) (hrs)	-
Comparative Example 6 (Molded Article V)	
Injection Moldability	Molding was impossible.
Band Clamp Properties	
Band A Type	-
Band B Type	-
Life (band A) (hrs)	-

As is apparent from the results shown in Tables 2 and 3, the molded articles I to V in Examples 1 to 5, which were the joint boots obtained by injection-molding the thermoplastic polyester elastomer compositions in which the rubber is contained for the increase of flexibility, could be fixed by band A and had sufficiently long life as a joint boot.

On the contrary, the molded article VI obtained in Comparative Example 1 could not be fixed by band A. Furthermore, each of the molded articles I to V in Comparative Examples 2 to 6 could not be released from the mold while the shape of the boot was maintained, and they could not be fixed by band A.

CLAIMS

1. A joint boot manufactured by injection-molding a flexible thermoplastic polyester elastomer composition prepared by blending 20-99% by weight of a thermoplastic polyester elastomer and 80-1% by weight of a rubber.

2. A joint boot as claimed in claim 1, in which the modulus of tensile elasticity of the thermoplastic polyester elastomer composition is in the range of 30 to 400 kgf/cm^2.

3. A joint boot as claimed in claim 1, in which the tensile breaking strength of the thermoplastic polyester elastomer composition is in the range of 50 to 300 kgf/cm^2.

4. A joint boot as claimed in claim 1, in which the permanent compression strain of the thermoplastic polyester elastomer composition is 80% or less.

5. A joint boot as claimed in claim 1, in which the modulus of tensile elasticity, the tensile breaking strength and the permanent compression strain of the thermoplastic polyester elastomer composition are 30-400 kgf/cm^2, 50-300 kgf/cm^2 and 80% or less, respectively.

6. A joint boot comprising a bellows portion having valleys and crests between a large-diameter opening and a small-diameter opening, wherein each of which valleys and crests is formed by a slant face on a large-diameter opening side of a valley and a slant face on a small-diameter opening side of another valley adjacent thereto at angles which are substantially equal to each other between different valleys, and the ratio of the outer diameter of a crest on the large-diameter opening side to that of another crest adjacent thereto on the small-diameter opening side is in the range of 1 : 1.0-0.50.

7. A joint boot as claimed in claim 6, in which the number of the crests in the bellows portion is in the range of 4 to 9.

8. A joint boot as claimed in claim 6, in which the wall thickness of the bellows portion is in the range of 0.5 to 2.5mm.

9. A joint boot as claimed in claim 6, in which the number of the crests in the bellows portion is 4-9, and the wall thickness of the bellows portion is 0.5-2.5mm.

10. A joint boot constructed and arranged substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

11. A method of constructing a joint boot substantially as hereinbefore described with reference to the accompanying drawings.

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Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI

Documents considered relevant following a search in respect of Claims :-
1-5

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 2122627 A	(SHELL) Claim 1; page 2, lines 20-21; page 7, line 26	At least Claim 1
Y	EP 0294179 A2	(HOECHST CELANESE) Claim 1; page 2, lines 19-21	At least Claim 1
Y	EP 0101427 A2	(MONSANTO) Claim 1; page 1, lines 11-18	At least Claim 1
Y	US 4367316	(TANAKA) Claim 1; column 3, lines 15-23	At least Claim 1

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).